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DRAFT
SEDIMENT SAMPLING REPORT
NEW BEDFORD HARBOR SUPERFUND SITE
New Bedford, Massachusetts

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Prepared for
U.S. Army Corps of Engineers
New England District
Concord, Massachusetts

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TABLE OF CONTENTS

1.0 Introduction

Foster Wheeler prepared this Sediment Sampling Report to summarize the sediment sample results collected from New Bedford Harbor. The purpose of this report is to delineate PCB concentrations in harbor sediments for future harbor remediation activities.

PCB contamination in New Bedford Harbor is known to have originated as early as the 1940's. Since that time, PCB contaminated sediments have migrated throughout the upper, lower, and outer harbor via flow of the Acushnet River and tidal influence. During this time, the PCB Aroclors may have weathered from their original configurations due to environmental factors.

In the Record of Decision (ROD) for the site, EPA established several cleanup goals for the site to be protective of human health and the environment. Cleanup goals vary based on the geographical location and were established in part, to reduce the amount of PCBs that accumulate in seafood and may ultimately be consumed by humans. Cleanup goals were also established to be protective of local residents who live adjacent to the harbor and for areas accessible to beachcombing. Cleanup goals in salt marsh areas were established to be consistent with the remediation goals for the harbor and while minimizing disruption of the beneficial and productive wetland environment. Accordingly, PCB cleanup goals vary throughout the subtidal and intertidal areas based on the exposure scenario. PCB cleanup goals are summarized as follows:

In direct contact areas for residents and beachcombers:

1 ppm	In beach areas immediately adjacent to residential properties
25 ppm	In marsh areas subject to beachcombing activities

In other areas, primarily to reduce the risk to humans through the ingestion of seafood:

10 ppm	Shoreline to shoreline in the upper harbor with the exception of beneficial salt marsh and wetland areas
50 ppm	In salt marsh areas not readily accessible to beachcombing and in the subtidal areas of the lower and outer harbor

PCB cleanup goals are defined in the ROD as total PCBs. Section 2.0 of this report summarizes the sediment and associated spilt sample collection procedures employed during the field program. Section 3.0 discusses key issues related to PCB analysis at New Bedford Harbor and the rational for the analytical methods that have been utilized in conjunction with this sampling effort. Section 4.0 summarizes the QC review and validation methods applied to the PCB analytical results. Section 5.0 briefly discusses the results of comparison evaluations of the PCB results and USACE QA data. The sediment sample PCB data set is presented in Appendix A. Site figures are presented in Appendix B and Northing and Easting coordinates in Appendix C. Appendix D presents individual QC data review memoranda and associated work sheets. The USACE QA reports results are presented in Appendix E.

2.0 Sample Collection and Procedure for Splitting Samples

Foster Wheeler collected samples from various locations throughout the harbor to further delineate areas of sediment above the ROD defined cleanup goals. Sampling locations were selected by EPA and USACE and were chosen to fill data gaps identified following earlier sampling events. Samples were collected in one-foot intervals from the mud line surface to depths of up to four feet, depending on the data need. Samples were identified sequentially by location with a suffix designating the bottom depth of the one-foot interval (i.e., -2 designates the 1 to 2 foot interval). Sample locations and results are presented in Appendix A. Site figures are presented in Appendix B. Northing and Easting coordinates are presented in Appendix C.

Samples were collected using various methodologies depending on the nature of the sediments. Equipment included a hand auger, manually driven split spoon, and vibracore sampler (used mostly for offshore locations accessed by boat). Equipment was selected to maximize sample recovery and ensure the representativeness of the depth interval being sampled. Samples were composited over the one-foot interval by mixing well in a disposable bowl with a stainless steel spoon. Following mixing, the sample was placed into the appropriate number of jars, depending on the analyses.

Approximately 1000 samples were collected during sampling. Samples were split at a frequency of one in twenty for QA/QC analyses (field duplicates, MS/MSDs, and USACE split samples analyses.

3.0 Analytical Methodology

3.1 Analytical Background

Conventionally, total PCBs have been determined using Aroclor analysis and are typically reported as the sum of detected Aroclors, especially when the Aroclors present on the site have been defined through earlier studies. Conventional Aroclor analysis is a gas chromatography method that identifies target analytes (Aroclors) using a "fingerprint" pattern recognition technique. The concentration of the Aroclor is calculated based on the size of individual chromatogram peaks (typically three to five peaks), chosen as representative of the specific Aroclor. PCBs in the sediments from New Bedford Harbor have been chemically degraded (weathered) over time and the Aroclor pattern has either changed to the point that the Aroclor quantification is no longer accurate or the pattern has degraded to where it is no longer recognizable.

Degradation processes can adversely affect the use of Aroclor analyses to characterize sediment PCB concentrations and subsequently to confirm that remediation clean-up goals have been achieved at New Bedford Harbor. In addition, other methods of PCB analysis (congener group analysis and /or homologue group analysis) are frequently used to analyze biological samples at New Bedford Harbor and elsewhere, thereby making direct comparison to Aroclor sediment data difficult. As a result, during this sediment-sampling program, a combination of Aroclor, congener and homologue group analyses were performed. Subsequently, the relationships between these alternate methods were compared and are discussed under a separate technical

report (see *Comparison of PCB NOAA Congener with Total Homologue Group Concentrations, New Bedford Harbor Superfund Site, April 2001*).

3.2 Analytical Methods

In the current study, samples were analyzed using the three analytical methods described below. The methods were selected following discussions with EPA, USACE, and Foster Wheeler Environmental.

Total Homologue Groups – This method uses gas chromatography (GC) in combination with low-resolution mass spectrometry (LRMS) to selectively identify and quantify PCB groups based on their specific mass. Results are reported for each homologue group (i.e., total mono through deca PCBs). The total homologue group method was expected to provide the most accurate measure of total PCBs as it reports PCBs by mass with minimal potential for falsely high data or missed compounds. The drawbacks to this method are that it requires highly specialized equipment, software, and highly trained analysts.

Aroclors – Aroclor analysis is a gas chromatography/electron capture detector (GC/ECD) analysis that identifies the Aroclor mixture of congeners by retention time and pattern recognition. Target compounds are identified primarily by pattern recognition with the concentration confirmed using second column confirmation. Quantification is performed by external standard technique using three to five chromatography peaks that are representative of the Aroclor selected. As noted above, this is the conventional method for PCB analysis and the method used for much of the historical data collected from the harbor. The disadvantages to using this method are that more than one Aroclor is present in the harbor and they are, in some cases, heavily weathered. This method is also subject to interferences from non-target compounds. These method limitations pose difficulties both with identification and quantification creating the potential for falsely high results due to overlapping and/or interfering peaks and falsely low results due to mis-identification due to weathering or interferences.

Congener Analysis – Selected PCB congeners were analyzed using the same analytical method as that used for Aroclors (GC/ECD). The congener method identifies selected individual congeners (NOAA and WHO congeners) using retention time with second column confirmation for both identification and quantification. Because this method reports individual congeners based on retention time, false negatives due to weathering are minimized. This method is subject to potential false positives from target and non-target analytes (see Section 4.2 below). In some ways, this is more of a concern than for the Aroclor method because pattern recognition is not used to selectively choose peaks for quantification. On the whole, the effects of potential false positives on the total PCB concentration are minimized by the use of second column confirmation (the lower of the two values is reported).

3.3 Overall Analytical Approach

Congener analysis was selected as the primary analysis for this sampling event. The correlation study noted above, was performed to develop a relationship between congeners and homologue groups would become a part of a defensible means of performing total PCB analysis for the

lifetime of this project (possibly ten years or more). The congener method was selected as a cost effective alternative to homologue group analysis and less likely to mis-identify or mis-quantify PCBs due to weathering than Aroclors. This method could be relatively easily implemented in an on-site laboratory, should one be required at a later date, and is likely to remain consistent with analytical advances over the upcoming years.

Also note that, samples in residential (1 ppm cleanup goal) and beachcombing (25 ppm cleanup goal) areas were analyzed for WHO congeners in addition to the NOAA congeners. This data will be available to determine the significance of the WHO congeners relative to total PCBs and available to develop a congener specific risk based cleanup goal in areas subject to human exposure, should one be required. The NOAA congeners are noted in the Sediment Sample Data Report tables, Appendix A, with an asterisk (*) in the BZ# column.

4.0 Data Review and Validation

The sediment PCB results were reviewed for compliance with analytical QC criteria to determine the acceptability of the overall data set and individual data points for use in achieving project objectives.

4.1 QC Review Approach

Data were given a "checklist" review for compliance with QC criteria. This review was based on the Region I, EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses, December 1996 criteria, and was intended to identify significant QC exceedences which may significantly affect the reported sample results. This brief review was intended to provide information on the quality of the data in more detail than an EPA Region I Tier I validation, but was not intended to provide as much detail as a Tier II validation. This data review included an evaluation of the following QC measures:

Data Completeness
Sample Preservation and Technical Holding times
Blank Analysis
Field Duplicates
Matrix Spike/Matrix Spike Duplicate
Surrogate Compounds
Initial Calibration
Continuing Calibration
Laboratory Control Sample

In developing the approach for overall data QC evaluation, the checklist review was chosen to provide cost effectiveness and also to develop a procedure that could be implemented on a faster schedule than a complete Tier II validation. An expedited schedule was not of primary importance for the current sampling program. However, the intent was to develop the QC procedures that could be implemented on an expedited schedule during remediation, if required.

To ensure that the checklist review was effective in identifying QC exceedences, approximately 10 percent of the data were selected for an EPA Tier II validation. The choice of samples for Tier II validation was left to the discretion of the reviewer and was intended to be flexible. If the results of the checklist review identified potentially significant QC exceedences, a Tier II validation would be implemented to further evaluate the exceedences. Similarly, if the Tier II validation identified systematic problems with the laboratory, additional review and or validation might be necessary to assess the effects to the entire data set.

The Tier II validation which was utilized included a review of the QC parameters listed above and also included an evaluation of the following:

Overall Evaluation of Data and Potential Usability Issues
Sample Quantitation
Target Compound Identification
Surrogate Retention Time Check
Target Compound Identification
System Performance

Data review memoranda and worksheets are presented in Appendix D.

4.2 Sediment Sample QC Results

The data review process identified some systematic difficulties (discussed below) that did not require further investigation with a complete Tier II validation. With input from EPA and USACE, the sample results selected for Tier II validation were biased toward sample results from residential areas that indicated the potential for a risk to human health (results that exceeded the 1 or 25 ppm criteria).

The results from the data reviews and validations are reported in the data review memoranda in Appendix B. The data review identified two significant findings with the data relative to the use of these sediment sample results. These are summarized below:

In the majority of cases, field duplicate results met the 50 % RPD criteria defined by the EPA Region I data validation guidelines as acceptable for soil/sediment precision. In some cases, field duplicates did not agree well and no cause for the discrepancy due to laboratory methodology was identified from the review. The variability appears to be matrix related and is much more apparent with the higher concentration samples, which often require multiple dilutions prior to analysis. Sample homogeneity may also be a factor in this discrepancy.

The second significant QC finding affected the congener analysis and was identified in the initial calibration verification standard (ICV). This standard is used to verify the initial calibration of the instrument prior to sample analyses. Prior to October 18, 1999, the laboratory purchased a prepared initial calibration verification standard that included both target and non-target congeners. Some of these non-target analytes coelute with target analytes on the chromatography column causing a high recovery (up to 200%) for some of the target congeners. The laboratory was made aware of this problem and a new ICV standard alleviated the problem.

This finding does not have a direct affect on reported concentrations since the ICV is not used to calculate sample results. It does indicate that non-target PCB congeners could be present in some sediment samples, which would cause a falsely high or false positive result for a specific congener. For the purpose of determining total PCBs, it can be assumed that the ratio of non-target to target congeners is the same for each sample. Therefore, the potential bias is the same for each sample and would be included in any ratio or correlation factor calculations. This should negate the bias in the total PCB value. However, should congener data be used for risk assessment calculations where the risk factors are dependent on the chemical characteristics of the individual congeners, it is important to consider that certain reported values could be biased high. If the data were to be used for a congener based risk assessment, it may be appropriate to consider a more accurate method of congener identification.

Other QC exceedences that were identified during the data review were relatively minor in nature, potentially affecting individual sample results and generally not applicable to the data set as a whole. Some of the QC exceedences were associated with poor matrix and surrogate spike recoveries, especially for high concentration samples. These appear to be related to the interferences from elevated concentrations of target and non-target analytes and, in some cases, the significant dilutions required to bring extract concentrations within the instrument calibration range. This type of QC exceedence is consistent with the earlier conclusion that the data are likely to more variable at the higher concentrations.

5.0 USACE Split Sample Comparison

As a measure of quality assurance, approximately three percent of the field samples were split and sent to the USACE designated laboratory (Phillip Analytical Services) for independent analysis. The split samples were analyzed for NOAA and, in some cases, WHO congeners using the same methodology as the primary laboratory (EPA Methods 3540C/8082). The Chemical Quality Assurance Report prepared by ENSR Corporation is attached in Appendix E. In summary, this report concludes that overall 90 percent of the individual results (including non-detects) were in agreement as defined by the USACE guidelines. These include the following:

- Both values are less than the respective detection limit
- One result is non-detect and the other is detected at a concentration less than the (other) non-detect value
- The results agree within a factor of 4

It is of interest that Phillip Analytical extracted seven samples using both sonication (EPA Method 3550B) and soxhlet (EPA Method 3540C) methods with varying results. The USACE prefers soxhlet extraction as a more complete extraction. ENSR reviewed the results in the context of agreement with the Severn Trent data and concluded that the extraction method did not affect the sample comparisons in a consistent manner.

In addition to ENSR's conclusion, it also appears that the extraction method does not necessarily correlate with concentration. Two samples had greater results using the sonication method and four samples had greater results using soxhlet extraction. Some sample results were more variable than others. This limited data set suggests that sample variability contributes more to

differences in reported concentration than the sample preparation method. This variability is consistent with the findings from the field duplicate results discussed above. USACE Chemical Quality Assurance Reports (CQARs) are presented in Appendix E.